

Cadmium in alkaline solution

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This review is intended to up-date the literature which has appeared since the previous article by Armstrong *et al.* [1] concerning the behaviour of the cadmium electrode in alkaline solution. In general the early literature will not be discussed since this is adequately covered elsewhere [2-7]. The wider aspects of the electrochemical behaviour of cadmium in various electrolytes can be found in the extensive review by Hampson and Latham [6].

1. Introduction

This review is subdivided into main sections as follows: Section 2: The composition and reduction of anodic films on cadmium; Section 3: Anodic behaviour of planar cadmium electrodes; Section 4: Cyclic charge-discharge behaviour of porous cadmium electrodes; Section 5: Long-term deficiencies of porous cadmium electrodes and Section 6: Theoretical studies concerning porous cadmium electrodes. Greater weight will usually be attached to the more technologically important aspects of Cd-electrode behaviour, with particular emphasis on the nickel-cadmium battery system.

2. The composition and reduction of anodic films on cadmium

In the past relatively few studies have been devoted entirely to consideration of the reduction of anodic films on cadmium. This is surprising in view of the importance of such processes in understanding the mechanism of charging of the cadmium electrode in alkaline battery systems.

2.1. Structural considerations of $\text{Cd}(\text{OH})_2$

As discussed in the review by Armstrong *et al.* [1] $\beta\text{-Cd}(\text{OH})_2$, $\gamma\text{-Cd}(\text{OH})_2$ and CdO can be present in anodic films on Cd and these materials have different structures. The term β -phase is commonly used

to describe both the poorly crystalline α -phase [1, 8], precipitated initially in alkaline solution, and also the well-crystallized β -phase having defined lattice parameters ($a_0 = 349.6$ and $c_0 = 470.2$ pm) [8]. Both α - and $\beta\text{-Cd}(\text{OH})_2$ belong to a hexagonal layer lattice system of the C6 type (Brucite). It is in principle possible for the unstable α -phase to have a greater degree of hydration than $\beta\text{-Cd}(\text{OH})_2$ and to exhibit a variable and increased interlayer spacing due to the presence of H_2O between the OH^- anion planes. Such structures are analogous [9] to those of α - and $\beta\text{-Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$.

Because of the inherent tendency of layer lattices to show differences in the stacking sequence between the layers a variety of secondary structures can be exhibited by the β -phase which shows differing conductivity and electrochemical properties, as discussed by Appelt [10, 11]. On the other hand $\gamma\text{-Cd}(\text{OH})_2$ has a crystal structure entirely different from the Brucite type [8, 12]. According to de Wolff [12] the γ -phase is monoclinic with four molecules per unit cell with lattice parameters of $a_0 = 567$, $b_0 = 1025$ and $c_0 = 341$ pm. Water is not required as an integral part of the structure as in $\alpha\text{-Cd}(\text{OH})_2$.

In dynamic electrochemical experiments, $\gamma\text{-Cd}(\text{OH})_2$ is sometimes invoked as the 'active' phase without supporting data from X-ray studies or i.r. spectroscopy. It is more likely in some cases that the differences in cathodic behaviour are due to subtle differences between the β -phase materials.

Because of the rapid conversion of the α -phase in strong base [13] and its poor crystallinity, the latter has not been well characterized. Nevertheless, α -Cd(OH)₂ is a possible short-term intermediate in the cyclic charge–discharge behaviour of the cadmium electrode, and could give rise to enhanced solubility before ageing to β -Cd(OH)₂, as will be apparent later in this review.

2.2. Mechanism of reduction of Cd(OH)₂ and CdO

Certain authors [14–17] held the view that the reduction of Cd(OH)₂ takes place by a solid-phase process whereas others [18, 19] have proposed soluble intermediates. Both Breiter and Vedder [20] and Okinaka and Whitehurst [19] have demonstrated, using X-ray diffraction, the presence of monoclinic γ -Cd(OH)₂ in addition to the normal hexagonal β -phase in anodic products. The γ -phase is found to be most stable at low temperatures but appears to reduce more readily at both ambient and low temperatures [19].

Using a rotating disc electrode Okinaka [21] found evidence for both solid-phase and solution-phase transport of cadmium species, with the contribution from the solution species assuming greater importance as the reduction progressed. Will and Hess [22] have examined the cyclic charge–discharge behaviour of a so-called ‘simulated single pore electrode’ (essentially planar) obtained by electrophoretic deposition of CdO (10–400 μm thick) on a copper substrate. It was claimed that charging took place at low over-potential and provided evidence for a solid-state reduction process. The large Cd(OH)₂ crystallites (mainly β -phase) formed during the early stages of cycling were found to be difficult to recharge (via soluble intermediates) except at low current densities and after prolonged times. Some γ -Cd(OH)₂ was also in evidence and was presumably formed via rehydration of CdO (see Section 2.3).

Armstrong and West [23], employing cyclic voltammetry in conjunction with a Cd rotating disc electrode in 10 M KOH, found that during the early cycles the charge recovered on the cathodic sweep was only approximately one-third of that used in the anodic process. As cycling progressed the anodic and cathodic peak areas (charge) became more equivalent. It was suggested, reasonably, that the reduction peak at -960 mV with

respect to Hg/HgO was due entirely to reduction via a solid-phase reaction since the voltammograms changed little with the rotation speed of the electrode. It was concluded from the decline of the anodic peak area on cycling that unreduced Cd(OH)₂ film remained on the disc, indicating a marked inefficiency in the reduction process. However this explanation tends to underestimate the important part which soluble intermediates, e.g. Cd(OH)₄²⁻, can play in the reduction process in an unstirred electrolyte, which in reality is more appropriate to the battery environment.

Galushko *et al.* [24] have re-examined the conditions under which CdO can be formed on a cadmium surface. It was shown that the colour of the anodized layer changed from light grey to black and then to yellowish black with increase in temperature, electrolyte concentration and current density. X-ray diffraction measurements (no data presented) were claimed to indicate that the yellow layer consisted of Cd(OH)₂ whilst the black layer contained both Cd(OH)₂ and CdO. During anodization of Cd at 70–80° C fluctuations in potential were observed due to disruption of the film by oxygen and its repassivation. It was claimed that anodization in 2 N KOH at 80° C at a current density of 2–4 mA cm⁻² in the oxygen evolution region was suitable for generating oxide-containing layers.

Continuing their previous investigations Galushko and co-workers [25] studied the reduction of heavily anodized films on Cd. The galvanostatic reduction of the film was performed over a range of alkali concentrations (0.1 to 10 M) and current densities (1–12 mA cm⁻²). These workers observed a main charging plateau (as expected) near -800 mV NHE (~ -900 mV with respect to Hg/HgO) with a more diffuse second plateau extending to -1200 mV NHE. A third plateau at -1.3 V was found and a clear explanation not given, but it is suggested that it may be due to formation of intermetallic compounds between Cd and K⁺ or, even less likely, to the formation of a hydride. Galushko *et al.* [25] considered that the low potential plateau is due to reduction of both CdO and Cd(OH)₂ because these phases were detected by X-ray diffraction (data not presented). Because the Cd/CdO/KOH couple has a standard potential of -765 mV compared with -810 mV NHE for Cd/Cd(OH)₂/KOH it ought to

be possible to distinguish between the two processes. For example, previous workers [21, 26] have identified by voltammetry a small prewave attributed to CdO reduction at ~ -775 mV with respect to NHE before the main reduction peak at -840 to -860 mV NHE. From the galvanostatic results presented by Galushko *et al.* [25] it is difficult to differentiate between the CdO and Cd(OH)₂ reduction processes. These workers concluded that the reduction process proceeded by a solid-state mechanism because of the invariance of the charging curves to stirring of the electrolyte (unspecified convective conditions).

In a further paper Galushko *et al.* [27] found at 80°C and low current densities that the initial step at -800 to -810 mV NHE was very small in 0.1 and 1 M KOH and totally absent in 10 M KOH. This was considered to be consistent with the lack of passivation of Cd anodes at low current densities and high temperatures (80°C). The process taking place at both 20°C and 80°C at higher potentials in the range -1100 to -1250 mV NHE, which represented $\sim 50\%$ of the anodic charge, was not studied in detail. It was postulated that the first plateau was due to reduction of both CdO and an 'active' γ -Cd(OH)₂ whilst at higher potentials an inactive β -phase was invoked. The involvement of γ -Cd(OH)₂ in the reduction process at temperatures as high as 80°C is unlikely, although it may have been present in small amounts at 25°C.

Later studies by Galushko *et al.* [28] involved a voltammetric sweep technique. Two maxima were observed on reduction of the anodic films at -935 and -975 mV with respect to Hg/HgO in both 4.5 and 10 M KOH. The first maximum was found to increase with increasing potential of anodization up to -500 mV. Furthermore, when the potential of anodization reached visible oxygen evolution ($+1350$ mV) a new peak at -1400 to -1500 mV appeared in the reduction process. In 10 M KOH the third peak tended to be smaller than observed in 4.5 M KOH whilst the first maximum increased. It was suggested that the peak at -1400 mV may be due to reduction of cadmium peroxide.

In a further paper these workers [29] attempted to provide confirmation of the third peak. It was found that a sample of chemically prepared CdO₂ · H₂O reduced on a Cd substrate at -1440 mV in agreement with their hypothesis.

The remarkable stability of the peroxide was explained by the lower heat of atomization of Cd (26.97 kcal/g atom) compared to that of oxygen (159.16 kcal/g atom).

The possibility of the involvement of peroxide and related species in the passive film on cadmium is supported by the electron spin resonance studies of Casey and Gardner [7]. These workers have been able to detect the presence of the paramagnetic ions O₂⁻ and O₃⁻ in the electrolyte removed from the surface of a cadmium electrode operating in the oxygen evolution region. In the range $+25^\circ$ C to -25° C the superoxide ion O₂⁻ can be found whilst at lower temperatures (-40° C) the ozonide ion O₃⁻ is the only species which can be detected. Although this work can give no clarification as to whether CdO is present in the initial stages of passivation, the detection of oxygen intermediates implies that the underlying film is electronically conducting.

Udupa *et al.* [30] consider that reduction of lightly compressed CdO powder takes place predominantly via a solid-phase mechanism in low concentrations of NaOH (< 5 M). At higher concentrations of alkali, evidence was obtained for the involvement of soluble intermediates from the increased crystallite size of the resulting Cd metal. The distinction between the operation of a dissolution-precipitation and solid-state mechanism of charging was made on the basis of the insensitivity of the latter process to stirring of the electrolyte. However, because an essentially porous electrode structure was being considered, the effective diffusion path length for cadmate deposition would be considerably smaller than for a planar case in the absence of solid material on the electrode surface. Thus relatively high rates of convective diffusion would be needed to distinguish with certainty between the two mechanisms. Nevertheless, the overall conclusions reached by Udupa *et al.* are probably valid.

Obedkov and L'vova [31] have similarly investigated the reduction of films formed on cadmium at high anodic potentials (oxygen evolution). The reduction of the film was made galvanostatically over a range of current densities (0.05–500 mA cm⁻²) in a range of alkali concentrations (1–8.1 M KOH) at 20°C, and in 8.1 M KOH at 60 and -40° C. In 8.1 M KOH at 20°C it was found that ~ 30 –50% of the products were reduced with an

overpotential less than -100 mV. The reduction of the remaining $\text{Cd}(\text{OH})_2$ was found to take place at much higher overpotentials of -500 mV. At moderate current densities (5 mA cm^{-2}) a total equivalence ($\pm 3\%$) between the anodic and cathodic processes was found. At lower current densities ($0.25\text{--}2.5 \text{ mA cm}^{-2}$) a discrepancy of $10\text{--}20\%$ was found where the cathodic charge recovered was greater than the anodic charge supplied. This suggests that cadmate was present in the bulk of the electrolyte prior to the measurements. At low current densities ($\sim 0.25 \text{ mA cm}^{-2}$) no separation between the $\text{Cd}(\text{OH})_2$ and H_2 evolution process could be made.

At low temperatures (-40°C in 8.1 M KOH) and at ambient temperature in 1 and 2 M KOH the first reduction plateau was considerably shortened to $2\text{--}5 \text{ mC cm}^{-2}$. It was concluded that this plateau related to the reduction of CdO passivating layers by a solid-state process. The extension of the first plateau in 8.1 M KOH at 20°C was considered to be due to reduction of an 'active' $\text{Cd}(\text{OH})_2$ via soluble intermediates. Accordingly the higher potential plateau was assigned to reduction of an 'inactive' $\text{Cd}(\text{OH})_2$. The involvement of soluble intermediates at the potential of the first plateau was confirmed by using electrolytes such as 0.1 M KOH or ethanol saturated with LiCl in which the cadmate species are less soluble or non-existent.

Potentiostatic and potentiodynamic studies by these workers [32] demonstrated that the first part of the film reduced at 0 V with respect to $\text{Cd}/\text{Cd}(\text{OH})_2$, indicating the presence of $3\text{--}4 \text{ mC cm}^{-2}$ of CdO in the passive film ($3\text{--}4$ monolayers). The reduction of the first part of the film at cathodic overpotentials of -20 to -100 mV demonstrated that a constant cathodic charge was involved. In comparison, at higher overpotentials (-200 and -500 mV) the reduction of the remaining film involved a variable cathodic charge and was strongly influenced by the H_2 evolution process. Limiting current densities for the reduction of $\text{Cd}(\text{OH})_2$ via soluble species were given as 16 mA cm^{-2} at $+20^\circ \text{C}$. These values seem to be at least two orders of magnitude too large on the basis of the earlier rotating-electrode work of Okinaka [21]. Calculations for a non-stirred solution using reasonable values for the saturation concentration of $\text{Cd}(\text{OH})_4^{2-}$ in 7 M KOH ($1.1 \times$

$10^{-7} \text{ mol cm}^{-3}$), the diffusion coefficient ($5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and the diffusion layer thickness (10^{-2} cm), indicate a limiting current density of $\sim 10 \mu\text{A cm}^{-2}$, i.e. three orders of magnitude smaller than those by Soviet workers.

Potentiodynamic studies by Obedkov and L'vova [32] revealed a complex dependence of the reduction peak heights with sweep rate. At low sweep rates the first peak at -100 mV with respect to $\text{Cd}/\text{Cd}(\text{OH})_2$ was found to be diffusion controlled. However, at higher sweep rates ($> 0.1 \text{ V s}^{-1}$) a limiting plateau was reached due to the inability of the chemical dissolution of $\text{Cd}(\text{OH})_2$ to be maintained. At very high sweep rates ($> 1 \text{ V s}^{-1}$) it is claimed that the first process corresponds only to the reduction of the passivating CdO layers ($1\text{--}6 \text{ mC cm}^{-2}$). The potential involved seems rather high for CdO reduction; nevertheless, a highly deficient semiconducting $\text{Cd}(\text{OH})_2$ could be considered as an alternative in the solid-state reduction process. The second cathodic reduction peak at -800 mV was considered to be due to a diffusion limitation in the solid-state at high sweep rates. However, the voltammetric data at high sweep rates (up to 60 V s^{-1}) is uncorrected for both ohmic drop and the effects of double-layer charging and such assignments must be viewed with some caution.

Obedkov and L'vova [33] have performed rotating ring-disc studies to clarify the nature of the reduction process (cf. earlier work by Okinaka [21]). The $\text{Cd}(\text{OH})_2$ formed on the pre-anodized disc was allowed to dissolve whilst the products were collected on the ring. Approximately 30% of the applied anodic charge could be recovered on the ring at a potential of -200 mV with respect to $\text{Cd}/\text{Cd}(\text{OH})_2$. The remaining hydroxide could only be stripped galvanostatically from the disc at -600 mV. It was found that the total charge registered on the ring together with that stripped from the disc was equivalent to the anodic charge supplied. The concentration of soluble species derived from the 'active' $\text{Cd}(\text{OH})_2$ was found to be $1.2\text{--}1.3 \times 10^{-4} \text{ mol dm}^{-3}$ in agreement with previously accepted values [1] for the equilibrium solubility of $\beta\text{-Cd}(\text{OH})_2$ in KOH . A diffusion coefficient for the cadmate ion was measured as $0.4 \pm 0.02 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, again in agreement with previous measurements [1]. The limiting currents found when the ring potential was -600 mV with

respect to $\text{Cd}/\text{Cd}(\text{OH})_2$ gave a value for the saturation concentration of the 'inactive' $\text{Cd}(\text{OH})_2$ of $1 \times 10^{-5} \text{ mol dm}^{-3}$, i.e. an order of magnitude smaller than for the 'active' variety. Further experiments revealed that when the products are reduced on the disc at the same time as the current is monitored on the ring, then once a certain disc current is reached no signal is registered on the ring. Thus complete capture of soluble species on the disc is also possible under suitable circumstances.

Barnard *et al.* [34] have similarly studied the reduction of $\text{Cd}(\text{OH})_2$ films on planar cadmium using slow cyclic voltammetry between the limits -750 to -1300 mV with respect to Hg/HgO . On the first cycle a single, broad cathodic peak at -945 mV was observed; however, on progressive cycling a second peak developed at -970 mV . The charge recovered on the cathodic sweep was considerably smaller than on the previous anodic sweep demonstrating the inefficient reduction of $\text{Cd}(\text{OH})_2$ on the planar surface. If the electrode was held at a potential in the passive region (-750 mV for 1 h) prior to the cathodic sweep then a small shoulder at -915 mV was observed on the main reduction peak at -960 mV . If the electrode was held at even more anodic potentials for longer times (-300 mV for 3 h) the prewave became more pronounced and appeared nearer -900 mV . In agreement with other workers [21, 26, 31–33] it is possible that the prewave indicates the formation of a thin layer of CdO beneath the main $\text{Cd}(\text{OH})_2$ layer.

In direct contrast to the planar electrode, sintered-plate electrodes [34] showed only a single broad anodic and cathodic voltammetric peak (at -840 and -970 mV with respect to $\text{Hg}/\text{HgO}/7 \text{ M KOH}$) with near equivalence between the anodic charge supplied and the cathodic charge recovered. This clearly demonstrates that charging of the sintered-plate electrode is considerably more efficient than its planar counterpart. It may be deduced that where soluble species are involved the sintered matrix provides a more effective collection system. There is possibly less tendency to form large $\text{Cd}(\text{OH})_2$ crystallites in the sintered-plate environment because of the increased number of nucleation sites afforded by the rough sinter interior. In addition there is more intimate contact between the active material and the current col-

lector which tends to assist a dissolution precipitation process by reducing the effective diffusion path length (the diffusion layer thickness would be expected to be less than the pore diameter, i.e. $< 10^{-3} \text{ cm}$).

In the case of the planar electrode the double cathodic reduction peaks might be related to the reduction of different types of $\text{Cd}(\text{OH})_2$. However this effect cannot be distinguished in the sintered-plate electrode. It is possible that the first cathodic peak relates to an 'active' α - or β - $\text{Cd}(\text{OH})_2$ having an enhanced solubility, whilst the second at higher cathodic potentials relates to well-crystallized β - $\text{Cd}(\text{OH})_2$. The presence of γ - $\text{Cd}(\text{OH})_2$ is less likely. Progressive ageing of β - $\text{Cd}(\text{OH})_2$ may also take place and this will be discussed in a later section.

The work of Barnard *et al.* [34] was unable to confirm the presence of highly unreactive $\text{Cd}(\text{OH})_2$ which might reduce at high cathodic potentials (about $-1.5 \text{ V Hg}/\text{HgO}$) as proposed by Soviet workers. Since the electrodes were not anodized in the oxygen evolution, CdO_2 would not be expected. Further cyclic voltammetric studies by Barnard [35] have qualitatively confirmed the earlier observations of Armstrong and West [23]. For example, for a Cd disc electrode rotating at 750 rpm and a voltammetric scan rate of 250 mV min^{-1} between the limits -800 to 1300 mV with respect to Hg/HgO , the anodic charge on the first cycle amounts to 87 mC cm^{-2} whilst that recovered on charge is only 27 mC cm^{-2} (cf. also Obedkov and L'vova [31–33]). On the 4th cycle the anodic charge is only 15 mC cm^{-2} . However, if the electrode is operated in a restricted electrolyte volume under stagnant conditions then after four cycles the anodic peak area is identical to that on the first cycle and almost total equivalence between the anodic and cathodic charges is retained (87 mC cm^{-2}). This implies that under suitable convective conditions soluble species can be recovered on the disc and moreover can in fact deposit on top of unreduced passivating hydroxides or oxide, effectively regenerating the original Cd surface area.

This curious behaviour suggests that the passive film formed on cadmium must have a high measure of electronic conductivity to allow the solution phase redeposition to operate. Evidence for electronic conductivity of the passive film has

been afforded by the ease with which oxygen can be reduced on its surface [23].

2.3. Transformation of CdO in alkali

Many of the objections [1, 7] to the presence of CdO in the passivating film stem from the well-known rehydration of CdO to Cd(OH)₂ in alkaline solution. Although this reaction is thermodynamically spontaneous it is by no means instantaneous, particularly in dilute alkali. Ea and Niepce [36] have recently studied the vapour-phase rehydration of CdO. When the oxide is pure rehydration is very slow but impurities considerably accelerate the process, ranking in the order KOH > KI > KBr > KCl.

Kadnikova *et al.* [37] demonstrate as expected that in concentrated alkali (5–12 M KOH) conversion of CdO to β-Cd(OH)₂ occurs extensively after 5 minutes (sharp band at 3605 cm⁻¹ in the i.r. spectrum). However, X-ray diffraction studies indicated the presence of unconverted CdO even after 24 h. In dilute alkali (0.1–3 M) the initial product of hydration appears to be γ-Cd(OH)₂ which could be detected by i.r. spectroscopy from the stretching vibrations at 3582, 3525 and 3284 cm⁻¹. The presence of low-frequency bands at 933 and ~960 cm⁻¹ conclusively prove the presence of hydrogen bonding which can only be present in the γ-phase (cf. Breiter and Vedder [20]).

Kadnikova *et al.* [38] have also studied the influence of conditions of hydration of CdO on its subsequent electrochemical reactivity. The effects of NiSO₄ additives were also examined. The main product of hydration of CdO in 1 M KOH was again found to be γ-Cd(OH)₂ whereas in water or 8 M KOH β-Cd(OH)₂ was the main product. In the presence of NiSO₄, β-Cd(OH)₂ predominated irrespective of the alkali concentration. Antimony oxide was found to retard the hydration of CdO. It was claimed that the highest level of Cd generation on charge and the highest current efficiency are attained when the level of hydration of the product is lowest or when the γ-Cd(OH)₂ is at a maximum. These results could be interpreted in terms of the charging of γ-Cd(OH)₂ taking place by a solid-state route. The galvanostatic charging plateaux were found to be at the lowest potential, where the level of hydration was lowest. In this respect electrodes prepared in the presence of

Sb₂O₃ showed the lowest charging potentials whilst electrodes hydrated in the presence of NiSO₄ charged at much greater cathodic potentials. It was noted that electrodes hydrated in 8 M KOH had low charge-acceptance behaviour because of the marked ageing of the β-Cd(OH)₂ formed.

In a recent communication, Breiter [39] has presented u.v. spectroscopic data to further substantiate the formation of CdO on thin Cd films deposited on a glass surface after prolonged anodic oxidation at low overpotential in 1 M KOH. The CdO was detected by its 2–3 eV adsorption edge, characteristic of the semiconducting oxide. Both β- and γ-Cd(OH)₂ were also detected by i.r. spectroscopy in the film. In more concentrated alkali (6.9 M KOH) very little CdO was found, the predominant phase being β-Cd(OH)₂.

2.4. Solid-state studies on CdO

The electrical conductivity of polycrystalline n-type CdO has been re-examined by Choi *et al.* [40] over a range of temperature from 298–923 K. Plots of log σ versus *T* at constant partial pressure of oxygen are found to be linear. The conductivity σ was found to be proportional to $P_{O_2}^{-1/6}$. A conductivity of 800 Ω⁻¹ cm⁻¹ was found at 300 K ($P_{O_2} = 1.2 \times 10^{-5}$ mmHg). The sign of the slope of the log σ versus *T* plot was found to change at ~673 K. This was explained in terms of increasing numbers of free electrons being scattering by those from the stoichiometric excess of Cd in interstitial positions or from oxygen donors.

The detrimental effect of Ca²⁺ on the charge efficiency of the negative electrode of the nickel–cadmium cell is generally well known [3, 10]. Rozovskii *et al.* [41] have again confirmed that as little as 0.02% Ca²⁺ has a marked degradation on the charge capacity of a CdO electrode. These workers consider that Ca²⁺ ions lower the charge acceptance of CdO by reducing the mobility of Cd²⁺ in the solid state. The conductivity of the CdO was deduced from potentiostatic *i* versus $t^{-1/2}$ plots during reduction in aqueous KOH. Arrhenius activation energies for the Cd²⁺ migration were claimed to be dependent on potential for pure CdO (16.5 kcal mol⁻¹ at -1.0 V and 5.06 kcal mol⁻¹ at -1.2 V with respect to Hg/HgO). In the case of CdO doped with 1% Ca²⁺ the activation energy was independent of potential

at potentials > -1.2 V, having a value of 9.2 kcal mol⁻¹. The values of activation energy determined by Rozovskii *et al.* infer a remarkably high mobility of Cd²⁺ in the solid state as would be expected for fast ion conductors. For example Haul and Just [42] have measured the enthalpy of movement of defects in dry CdO to be about 62 kcal mol⁻¹ at 630 – 850° C. It is possible that Rozovskii *et al.* [41] may have neglected the possible involvement of soluble cadmium species in their measurements.

2.5. Hydrogen evolution on Cd

Kukk *et al.* [43] have made a detailed study of the hydrogen overpotential on Cd in various alkaline media (NaOH, KOH, KOH + KCl, CsOH + CsCl and Ba(OH)₂). Hitherto this has been a rather neglected area of research [2] in spite of its technological interest. The paper by Kukk *et al.* [43] may be consulted for an assessment of the previous literature on the subject. Generally a Tafel slope parameter b , of ~ 118 mV/decade, is obtained over about four decades of current. The transfer coefficient α is taken to be 0.5 . From the dependence of hydrogen overpotential with alkali concentration it is deduced, in good agreement with theoretical considerations, that a slow direct discharge of water molecules is involved. In the case of Ba(OH)₂ electrolyte some evidence was found for an intermediate chemical step. The changes in overpotential in the different media were considered to be caused by variations in the electric field in the vicinity of the double layer caused by the present of ions of differing size.

The discharge of Na⁺, K⁺ and Cs⁺ ions to form intermetallic compounds was considered to be possible on rough Cd surfaces. However, the discharge of these species on smooth Cd was considerably delayed and was not thought to be the main cause for the differences in overpotential.

2.6. Conclusions

In conclusion it appears that α -, β and γ -Cd(OH)₂, together with CdO₂, may be present at the time of cathodic reduction, depending on the anodic history of the electrode. Any α -Cd(OH)₂ formed initially is likely to be converted fairly rapidly in strong alkali to β -Cd(OH)₂. At low temperatures

γ -Cd(OH)₂ can be a predominant phase. In order to obtain CdO, high anodic potentials (at least 200 mV more anodic than the reversible Cd/Cd(OH)₂ potential) are required. If the electrode is operated in the region of continuous oxygen evolution CdO₂ may also be formed.

Reduction of the various cadmium species appears to involve a complex combination of solid-state and dissolution precipitation processes. Active α -Cd(OH)₂ (possibly having an enhanced dissolution rate because of its smaller crystallite size) and normal β -Cd(OH)₂ with a low electronic conductivity are most likely to change via soluble intermediates. On the other hand cadmium hydroxide phases having defective structures (i.e. a stoichiometric excess of Cd in the lattice) and exhibiting semiconductivity could charge by both solid-state and soluble intermediates. There is evidence to suggest that the reduction of these semiconducting phases is often incomplete and Cd deposition via soluble intermediates may proceed on the surface of such materials leading to hydroxide occlusion. Semiconducting CdO appears to charge preferentially via a solid-state mechanism when the influence of secondary products derived from its immersion in KOH are neglected. At room temperature γ -Cd(OH)₂ is most likely to be derived from CdO in dilute alkali (< 7 M) whereas at high alkali concentration (7 M) β -Cd(OH)₂ predominates. It is possible [38] that γ -Cd(OH)₂ might charge by a solid-state mechanism; however, this has not been unequivocally demonstrated.

3. Anodic behaviour of planar cadmium electrodes

Since the previous review by Armstrong *et al.* [1] comparatively few papers have dealt with the mechanism of passivation of the cadmium electrode in alkaline solution. Previously [1, 7] there appeared to be a large number of papers proclaiming the relative merits of the dissolution–precipitation model of electrode failure compared with the solid-state mechanism. Largely as a result of the extensive work by Armstrong *et al.* [1] there now appears to be little doubt that the underlying film (either Cd(OH)₂ or CdO) causing passivation forms by a solid-phase mechanism. Nevertheless, the importance of the dissolution–precipitation process on both charge and discharge should not be overlooked, particularly

when considering the operation of sealed secondary battery systems. As pointed out by Milner and Thomas [2] the negative electrode in the nickel-cadmium cell, because of cell design constraints, seldom operates in the passive region except when excessively high discharge rates are used or when cell reversal has occurred. Thus for the most part, dissolution-precipitation processes have probably greater importance than solid-state mechanisms in determining the long-term recrystallization and redistribution of active material which takes place during the cyclic operation of porous cadmium electrodes. Nevertheless, to understand all aspects of electrode behaviour over wide anodic limits neither mechanism can be considered in isolation. (See also Casey and Gardner [7]).

Yarvaslu *et al.* [44] have studied the passivation of Cd in relation to its application in O₂ concentration gauges using various alkaline media, pH 15.2–8.2 (KOH, K₂CO₃, Na₂CO₃, KHCO₃ and mixtures). In all cases a linear dependence of passivation charge Q and $\log i$ (i is the galvanostatic current) is found. There is some deviation at higher current densities. It is claimed that the presence of Na⁺ ions lowers the passivation charge due to stabilization of the film by this ion. The $\log i$ - Q dependence is considered to indicate that passivation of the electrode is dependent on the diffusion of OH⁻ ions through the surface of the developing Cd(OH)₂ layer. The dependence of the passivation on electrolyte environment is related to the well-known involvement of complex ions in the anodic dissolution process. The effects of adding further complexing agents, e.g. Trilon B, SCN⁻ and PO₄³⁻ increased the charge before passivation because of increased Cd²⁺ complexing. However, SCN⁻ caused a decrease due to insoluble film formation. It is implied that the passivation process is controlled by a dissolution-precipitation mechanism; however, as discussed at length by Armstrong *et al.* [1] simple measurements of this type can give no information regarding the mechanism of formation of the underlying film.

From the shape of the potentiodynamic and chronoamperometric curves L'vova *et al.* [45] propose a mechanism of passivation involving adsorption of OH⁻ ions. The distinction between irreversible adsorption and a passivation process is difficult to make on the basis of the limited data presented. The interpretation of previous

impedance data [46, 47] by the same authors, and based on the same hypothesis, is open to considerable doubt [1].

Oshe *et al.* [48, 49] have returned to the important question of whether passivation could be caused by a very rapid dissolution-precipitation process rather than via the solid state. In rotating ring-disc experiments these workers find a lack of agreement between the theoretical and experimental collection efficiencies. This is considered to be due to incomplete detection of soluble species on the ring due to precipitation as Cd(OH)₂ on the spacer between the ring and disc (or on the disc alone) as a consequence of a rapid dissolution-precipitation reaction. Such a mechanism is offered as an alternative to that preferred by Armstrong and West [23] proposing 'leakage' of current via a solid-state route. Clearly, the use of very high rotation speeds would be required to distinguish with certainty between the two mechanisms.

Kravtsova *et al.* [50] have studied the influence of KOH concentration on the passivation behaviour of Cd. This work appears to be largely a repetition of earlier studies, in particular of the type by Farr and Hampson [51] demonstrating that the current density i and time to passivation t obey a relationship of the type $it^{1/2} = \text{constant}$. Kravtsova *et al.* [50] propose a modified expression where $t = Ai^{-n}$ and $n = 1.6$. The time to passivation is claimed to vary linearly with alkali activity. The mechanism of passivation is considered to be of the dissolution-precipitation type.

In a later paper Kravtsova and Zytner [52] investigated the effect of NH₃ as a complexing agent on the passivation time of Cd in alkaline solution. The passivation time was found to increase significantly only when the NH₃/KOH concentration ratio was greater than unity. This is due to the interplay between OH⁻ ions and NH₃ molecules in the complexing process. The increased passivation time is considered to be related to formation of ammines of the type $[\text{Cd}(\text{NH}_3)_x(\text{OH})_y]^{2-y}$ in dilute alkali whilst complex ions of the type Cd(OH)₄²⁻ predominate in concentrated alkali. Although there appears to be little doubt of the ability of complex-ion formation to extend the active dissolution region, these measurements shed no light on the final cause of passivation.

Afanasev *et al.* [53] have studied the electro-oxidation of Cd in 1 M KOH at rotating disc electrodes using a potentiostatic method. Regretably these workers treat the data erroneously in terms of

$$i_a = i_\infty + K\sqrt{\omega} \quad (1)$$

rather than with the correct expression of the form [23, 54]

$$\frac{1}{i_a} = \frac{1}{i_\infty} + \frac{K}{\sqrt{\omega}}. \quad (2)$$

From the potential dependence of the i_a versus $\sqrt{\omega}$ plots, a dependence of $\Delta E/\Delta \log i_a$ of 25 mV/decade (cf. the theoretical value of 29 mV) was claimed. The passivation behaviour is interpreted in terms of a dissolution-precipitation reaction taking place on a limited number of active sites on the electrode surface. It is interesting to note that in a similar study Armstrong and West [23] were unable to obtain satisfactory data for the dissolution process in 1 M KOH.

Armstrong and Edmonson [55] have made a detailed study of the impedance of planar Cd electrodes in alkaline solution. In the active dissolution region (-895 mV with respect to Hg/HgO/KOH), at frequencies ≥ 3 Hz, a Warburg impedance is found due to diffusion of soluble $\text{Cd}(\text{OH})_4^{2-}$ species. At very low frequencies (1.5 to 0.005 Hz) deviation is observed due to interaction of the Nernst diffusion layer with the a.c. diffusion layer. The data are treated on the basis of a simple Randle's circuit. From plots of R_p and C_p versus $\omega^{-1/2}$ the solubility of $\text{Cd}(\text{OH})_4^{2-}$ in 10 M KOH is estimated as $2-5 \times 10^{-4}$ mol dm $^{-3}$. A Nernstian slope of 30 ± 5 mV/decade for a 2e reversible reaction was confirmed from plots of $\log \sigma$ versus E . Estimates of the charge transfer resistance enabled the potential dependence of the exchange current to be deduced as 30 ± 5 mV/decade. This value was considered to be consistent with a reaction involving two consecutive electron transfers, the first being in equilibrium, the second rate determining. These observations entirely confirm the earlier observations made by Armstrong and West using a ring-disc technique [23].

A potential just into the passive region (-870 mV) showed Warburg impedance at high frequencies which was also rotation-speed dependent, similar to the observations in the 'active' region. This was interpreted in terms of diffusion of

soluble species in the film. At very low frequencies a second Warburg impedance was found due to diffusion of species within the solid phase. At potentials further into the passive region (-700 mV) a marked change in the shape of the impedance diagrams was evident, showing mainly a low-frequency Warburg impedance due to diffusion of species within the solid phase. This region showed very little dependence on the rotation speed of the electrode. It is curious to note that the 'solid phase' Warburg impedance at -700 mV appears at higher frequencies than at -870 mV. These observations clearly indicate that the nature of the film formed just at the point of 'passivation' (-870 mV) is different from that well into the passive region. It is tempting to suggest on the basis of observations previously discussed [34] that CdO may be developing under the $\beta\text{-Cd}(\text{OH})_2$ film formed initially. Diffusion coefficients for the species moving in the solid-phase were determined as $\sim 5.5 \times 10^{-10}$ cm 2 s $^{-1}$ at -870 mV and 5.1×10^{-12} cm 2 s $^{-1}$ at -700 mV. As the authors point out these values are only approximate because of diffusion-layer thickness constraints, nevertheless they do demonstrate the involvement of less mobile species in the solid phase during film thickening. An estimate of the passive film thickness was made ($400 \pm 20 \times 10^{-8}$ cm) from the charge required to reduce the passive film (~ 25 mC cm $^{-2}$). It should be noted that in this paper there are labelling errors. Fig. 12 relates to measurements at -700 mV and the headings on Figs. 14 and 15 should be transposed.

Barnard *et al.* [34, 56] have drawn attention to the presence of double anodic peaks during cyclic voltammetric studies of planar cadmium. The additional anodic peak at about 26 mV more cathodic than the main peak is considered to be due to the different behaviour of the electrodeposited Cd. Its more cathodic placement is considered to be related to intrinsic stress within the deposit due to occlusion of oxide or hydroxide. This observation correlates with the difficulty in completely removing the passive film.

Ojefors [57] has compared the potential-dynamic behaviour of Fe and Cd electrodes in alkaline solution over a range of temperature from 5 to 70°C. It is demonstrated that the iron electrode shows a greater dependence of the voltammetric peak current heights and position on

temperature than the cadmium electrode. This is thought to be due to the greater dependence of solubility on temperature for the intermediates (HFeO_2^- and FeO_2^-) involved in the operation of the iron electrode. Such differences are considered to account for the differences in performance between Cd and Fe.

Selanger [58] has discussed the influence of fast nucleation reactions on the shape of galvanostatic E versus t transients. A theoretical argument is presented which predicts the presence of a maximum at short times (~ 10 ms) in the case of electrodes such as Cd which involve sparingly soluble intermediates. The maximum is explained in terms of the fast build-up of dissolved species, which are in reversible exchange with the electrode, followed by a fast nucleation reaction in the supersaturated solution which consumes the dissolved species giving a decrease in concentration polarization.

Bonnaterre *et al.* [59, 60] have also compared the relative methods of operation of Fe and Cd anodes in alkaline solution. Considering only aspects of the Cd electrode, this work has again emphasized the importance of supersaturation of soluble cadmium species during anodic dissolution. Using a rotating ring-disc technique they have measured the supersaturation coefficient Γ of the cadmate ion over a range of temperature and in various alkaline concentrations. The value of Γ is given approximately by the ratio of the ring current response on reduction corresponding to anodic and cathodic sweeps on the disc. In 7 M KOH the value of Γ is 10.4 at 20°C. Although the equilibrium solubility of $\text{Cd}(\text{OH})_2$ in KOH increases with temperature the value of Γ decreases (i.e. 6.6 at 40°C). Although the values of Γ should ideally be independent of rotation speed, Bonnaterre *et al.* find some dependence on rotation speed. In contrast to previous rotating ring-disc studies [19, 21] the type of passivation mechanism is not considered.

4. Cyclic charge-discharge behaviour of porous cadmium electrodes

Interest has been renewed concerning the cause of capacity loss by porous cadmium electrodes during cycling. Earlier studies, in particular those by Harivel *et al.* [61], Salkind *et al.* [62], Lifshin and Weininger [63] and Breiter and Weininger [64],

have indicated the importance which growth and redistribution of active material play in determining cycle life.

Reed and McCallum [65] have made a detailed investigation of sintered-plate cadmium electrodes cycled to various depths of discharge. Electrodes were examined by metallographic techniques, and chemical analyses and capacity measurements in flooded electrolyte were made [66] to assess the relative charge and discharge efficiencies of active material. Greater losses of capacity were found at greater depths of discharge and greater cycle numbers. Much of the capacity loss was claimed to be temporary since a complete charge-discharge cycle was found to restore the capacity. The changes in capacity with cycling were found to be related to growth and redistribution of active material within the pore structure. Although uncharged $\text{Cd}(\text{OH})_2$ was found in the plates by chemical analysis ($\text{NH}_3/\text{NH}_4\text{Cl}$ extraction technique) there was often a discrepancy between the delivered capacities and analytical values, implying efficiencies greater than 100%.

Luksha *et al.* [67] have investigated the influence of nickel sinter structure on the performance of the cadmium electrode. Sinters having a controlled pore diameter were prepared using a pore former. Electrodes having a porosity of 80% and a pore diameter of 80 μm were considered to give the optimum performance. No correlation could be made between the sizes of the $\beta\text{-Cd}(\text{OH})_2$ crystals at the electrode surface (1–20 μm) and the pore diameter. This observation contrasts sharply with that claimed by Will and Hess [22] for a simulated pore electrode where growth of $\beta\text{-Cd}(\text{OH})_2$ is considered to be the main cause of capacity loss.

In the case of sintered plate electrodes Barnard *et al.* [56] have shown by chemical analysis that where the discharge rate is high ($C/1$) the loss in capacity during cycling was due largely to inefficient utilization of Cd metal rather than to an inefficient charge process. The quantity of Cd metal produced on charge was in the range 97 to 75% over the first 100 cycles. The level of unused Cd increased as the charge rate diminished being as much as 55% after ~ 90 cycles at the $C/8$ charge, $C/1$ discharge rate. A voltammetric sweep technique showed that this could be related to a progressive diminution of Cd surface area during

cycling which was most rapid at the $C/50$ charge rate. A decrease in the widths of the voltammograms suggested a redistribution of active material to the edges of the sinter during cycling giving pseudo-planar behaviour. Preliminary optical microscope studies confirmed the growth and redistribution of active material.

Further studies [34] showed that when low discharge rates were used, thereby increasing the cycle time, recrystallization of $\text{Cd}(\text{OH})_2$ could take place leading to a marked lowering in charge efficiency as determined by chemical analysis. The apparent independence of overall cycle efficiency on discharge rate, at a fixed high charge rate, observed previously [56] was due to an unexpected cancellation between the relative changes in charge and discharge efficiencies.

A failure mechanism, in line with that proposed earlier [68], was considered to involve coverage of the Cd surface by precipitated $\text{Cd}(\text{OH})_2$ which later induced a change in potential such that a passivating film formed directly on the surface by a solid-state process. The loss in capacity on cycling was considered to be due largely to growth of Cd metal crystallites leading to a lowering of active surface area. Nevertheless, under certain conditions, particularly where the cycle time was long (or periods of standing in the discharge state were involved) growth of $\text{Cd}(\text{OH})_2$ crystallites lead to a significant lowering in charge efficiency.

Papazova *et al.* [69] have investigated the influence of the initial charge current density (formation process) on the subsequent cyclic charge-discharge behaviour of pressed CdO electrodes for use in silver-cadmium cells. Chemical analysis revealed that the quantity of Cd produced during charging was about 95–98% after 2 cycles for changes in charge current density by over an order of magnitude. The utilization of active material on discharge after the first cycle was in the range 57–63% and was relatively insensitive to discharge rate. After 15 charge-discharge cycles it was found that electrodes 'formed' at 0.2 A dm^{-2} gave capacities of $\sim 50\%$ whilst those 'formed' at 0.8 A dm^{-2} gave capacities of $\sim 70\%$. It was concluded that the improvements were related to the production of a more finely divided cadmium at high rates of charge, in agreement with other workers [34, 56, 61]. It is interesting to note that the changes in capacity after the initial fall are much

less over 15 cycles than those observed by Barnard *et al.* [34, 56], and could reflect the obvious difference in electrode structure.

Papazova *et al.* [70] have similarly investigated steady-state potentiostatic E versus I curves as a means of assessing the performance of pressed Cd electrodes for use in silver-cadmium cells (cf. Armstrong *et al.* [68]). Generally, satisfactory quantitative agreement is found between the magnitude of the anodic peak current and the measured discharge capacity. The discharge capacity is shown to be increased by addition of $\text{Ni}(\text{OH})_2$ and also unspecified organic additives. Only partial correlation between the relative anodic peak heights and BET (argon) surface area measurements of the Cd powder was obtained. This was considered to be due to the lower apparent area seen in the electrochemical measurements due to the non-wetting (or non-involvement) of the smaller pores in the electrode operation.

Eron'ko *et al.* [71] have made a coulometric investigation of a cadmium electrode in alkaline solution. Little interpretation is offered. As the authors state, the technique has not been widely used due to experimental and interpretational difficulties.

Armstrong *et al.* [72] have made a detailed study of the impedance of a sintered-plate cadmium electrode after charge-discharge cycling. For a porous electrode with semi-infinite pores theory predicts that the phase angle of the impedance Z is half the value for an equivalent planar electrode whilst the absolute magnitude of Z is proportional to the square root of the planar electrode impedance. Thus, for a purely capacitive interphase, the impedance plot for a porous electrode would be a straight line at 45° in the Argand diagram (cf. the vertical line parallel to the imaginary axis for a planar electrode). Warburg diffusion in the porous electrode would give rise to a line having a slope of 22.5° (cf. 45° for the planar case).

For a porous electrode with semi-infinite pores the a.c. signal penetrates to only a limited depth at high frequencies whilst at low frequencies total penetration can occur. For example, in the capacitive case there is a critical frequency ω^* at which the impedance plot changes slope from porous to pseudo-planar character. The value of ω^* can be calculated from

$$\omega^* = \frac{r}{2\rho l^2 C_{dl}} \quad (3)$$

where r is pore radius, ρ the resistivity of the electrolyte, l the pore length and C_{dl} the double-layer capacitance. Impedance diagrams for fully charged sintered-plate electrodes at -1000 mV with respect to Hg/HgO show a slope of 37° at low frequencies changing to higher slope below ω^* (83 Hz). The presence of uncharged $\text{Cd}(\text{OH})_2$ in the electrode after cycling (10 cycles) could be detected from a small Warburg impedance (slope 24°) at higher frequencies. Differences in impedance diagrams could be detected for electrodes having different uniformities of impregnation. From the change in capacitance in the double-layer region (-1000 mV) the change in wetted surface area could be studied. As demonstrated previously [56] charging at low rates ($C/8$) gave rise to low surface area of Cd metal and this diminished on cycling.

In the passive region (-700 mV) the impedance diagrams were very similar to those obtained with planar Cd [55] when differences in area were taken into account. Nevertheless, the area of Cd apparently passivated was smaller than anticipated and it was suggested that only part of the Cd was being sensed because of screening of the a.c. signal by precipitated $\text{Cd}(\text{OH})_2$. An alternative explanation would be that only part of the Cd surface is passivated (cf. Okinaka [21]). From the measured Warburg coefficient a value for the diffusion rate of species within the passive film was calculated as $3.2 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ in agreement with values obtained [55] for the planar electrode.

The measurements of critical frequency were used to evaluate the depth of signal penetration and hence to compare the uniformity of impregnation of the electrode. However, the lengths calculated in fact exceeded the known sinter thickness. This is probably due to the choice of too large a value for the pore radius ($5 \mu\text{m}$) which excludes the contribution made by Cd. A more realistic value for the porous Cd network contained within the main sinter framework would be $0.5 \mu\text{m}$. It should be noted that the electrode half-thickness should have been employed in the calculation since the electrodes were not semi-infinite.

Barnard *et al.* [73] have made a detailed study, using optical and scanning electron microscopy, of

the growth and redistribution of Cd and $\text{Cd}(\text{OH})_2$ in sintered-plate electrodes as a function of charge rate and cycle number. The size of both Cd and $\text{Cd}(\text{OH})_2$ was found to increase with increasing cycle number and decreasing charge rate. On the other hand, high charge and discharge rates promoted greater aggregation and redistribution of active material towards the electrode edge. This was presumably caused by the greater non-uniformity of the reaction zones in the electrode at higher current densities. The trapping of Cd metal by highly crystalline, hexagonal platelets of $\beta\text{-Cd}(\text{OH})_2$ resulted in about 50% of the active material becoming obsolete after 100 cycles at high charge and discharge rates ($C/1$). At this stage only the finely divided Cd metal in the electrode interior continued to function. Because the deposits, particularly after extended cycling, invariably contained both components it was difficult to quantify their relative sizes. The pronounced redistribution and crystallization, particularly of $\text{Cd}(\text{OH})_2$, provides a clear demonstration of the operation of dissolution-precipitation processes. Evidence of a thin passivating hydroxide coating was also found.

Further SEM/optical microscopy studies [74] have revealed that Cd metal deposition can take place on top of conducting $\text{Cd}(\text{OH})_2$ (or CdO) crystallites, confirming that this process as a possible mechanism of active material occlusion (as discussed previously in Section 2.2). Marek *et al.* [75, 76] have similarly combined capacity, surface area, chemical analysis and electron microscopy measurements to study the influence of the impregnation process on the long-term cycling efficiency of sintered-plate Cd electrodes. The behaviour of electrodes prepared by thermal decomposition of cadmium formate was compared with those obtained by impregnation with cadmium nitrate. Electrodes obtained using a combination of these procedures were also studied.

It was found that electrodes prepared via cadmium formate alone gave poor reproducibility on charge-discharge cycling owing to shedding of active material and poor charge efficiencies arising from large CdO crystallites. Scanning electron microscopy showed for electrodes prepared by the other two methods that there was less tendency for $\text{Cd}(\text{OH})_2$ growth, suggesting a large number of nucleation sites. Chemical analysis revealed that

the higher capacities delivered by the plates prepared using the combined method arose from the increased charge acceptance. Generally electrodes having the highest surface area of active material gave the highest efficiencies. Morphological changes taking place in the electrode were considered to be largely the consequence of dissolution-precipitation processes, although partial involvement of solid-state processes could not be entirely dismissed (cf. Barnard *et al.* [73]). It is interesting to note that these authors have also developed a technique [77] for observing, with the SEM, the same point in a sintered-plate electrode during cycling. In general electrodes prepared using the combined impregnation method gave the lowest residual Cd contents after discharge and least agglomeration of active material in the electrode surface. A lower level of Ni²⁺ impurity (from sinter corrosion) was also found.

Little information is available concerning the use of organic additives to control the morphology of the cadmium electrode. Recently Udupa *et al.* [78] have found that the discharge efficiency of the sintered-plate cadmium electrode is improved when quaternary ammonium compounds such as cetyltrimethylammonium halides are incorporated in the active material at the time of impregnation. The improvement in discharge behaviour was considered to be due to the smaller size of the active material present in the plate. This hypothesis was deduced on the basis of low-magnification ($\times 150$) optical examination of active material removed from the electrode surface. Clearly, a more detailed study with higher magnification of active material in both the charged and discharge state would be desirable to provide a more convincing demonstration.

In earlier studies Gossenberger [79] made an evaluation of the behaviour of various cellulose and starch derivatives on the capacity of the cadmium electrode. It was tentatively suggested that growth of Cd metal was inhibited by the additives. Fleischer [80] subsequently patented the use of cellulose ethers and derivatives such as CMC for reducing the fall in capacity of the cadmium electrode on cycling. More recently Solo'eva and Ryzhok [81] mention the use of CMC and sunflower oil. This paper deals mainly with the preparation of samples from porous cadmium electrodes suitable for transmission electron micros-

copy. Organic additives frequently interfere in the determination of surface area (cf. difficulties encountered by Gossenberger [79]) and scanning electron microscopy provides a valuable method for assessing separately the growth of both Cd and Cd(OH)₂.

A recent paper by Jindra *et al.* [82] illustrates the trend towards the development of cadmium electrodes which do not require the use of expensive nickel sinter or the time-consuming impregnation procedures. Electrodes were obtained by pressing a paste of CdO and PTFE binder on to a current-collecting substrate. This type of electrode fabrication has been examined previously by Holleck *et al.* [83] and Luksha [84]. Relatively high levels of PTFE (5–20%) appear to have been used in the study of Jindra *et al.* [82]. This is perhaps surprising in view of the high hydrophobicity of PTFE and, as these authors discuss, its tendency to reduce the electronic conductivity of the matrix and create non-uniform distribution of current within the electrode structure.

By close packing of electrodes during cycling, shedding of active material and loss of mechanical strength can be substantially reduced and acceptable capacities are claimed over 700 cycles. The results suggest that the performance of thin, plastic-bonded cadmium electrodes are intermediate between those of the pocket-plate and sintered-plate fabrications.

Cenek *et al.* [85] have investigated the behaviour of plastic-bonded cadmium electrodes incorporating oxalic acid and a polyethylene binder on an iron substrate. It is claimed that the service-life of such plates is about 1900 cycles before the capacity falls to $\sim 46\%$ of its theoretical value. In order to obtain acceptable cycle life it is claimed that the plastic content should not exceed 30–35% by volume. The oxalic acid appears to be used mainly as a pore-forming agent, being leached out into the electrolyte on discharge. Scanning electron microscopy revealed that electrodes manufactured with oxalic acid additive formed smaller crystallites of active material compared to those without the additive. The structural changes within the active material were considered to be the main factors determining cycle life. Further studies by Cenek *et al.* [86] confirmed that incorporation of oxalic acid into the active mass increased the efficiency of utilization by

about 10–20% by minimizing active material aggregation.

5. Long-term deficiencies of porous cadmium electrodes

5.1. Long-term ageing

Whilst it is generally possible to operate the cadmium electrode between temperatures of -40°C and 70°C certain operational difficulties are encountered for example where it is required to operate the electrode at -20°C after long periods of storage at $+20^{\circ}\text{C}$ or $+70^{\circ}\text{C}$ [87, 88]. The earlier work of Okinaka and Whitehurst [19] clearly demonstrated that in order to minimize premature H_2 evolution during charging the first discharge should be made at the lowest temperature in order to facilitate formation of 'active' $\gamma\text{-Cd}(\text{OH})_2$ (see also Section 2).

Bramham *et al.* [89] have examined the recharge behaviour of both cadmium and nickel hydroxide electrodes removed from nickel–cadmium cells after storage (up to 5 years) in the discharged state. Scanning electron microscopy revealed considerable growth of hexagonal platelets of $\text{Cd}(\text{OH})_2$ on the electrode surface (trapping some of the separator fibres) which increased in size progressively with time. Hobbs *et al.* [87] have similarly observed the growth of $\text{Cd}(\text{OH})_2$ platelets on the surface of sintered-plate electrodes after 9 years' storage. In spite of this pronounced growth, galvanostatic measurements showed [89] that after ageing for 5 years, remarkably little deterioration in charge acceptance at 20°C had taken place for partial charge inputs at the 1 C rate. A decline in capacity at 20°C was noted however at very high charge rates (10 C). As expected the most noticeable deterioration in charge acceptance was exhibited where the $\text{Cd}(\text{OH})_2$ had been aged at 70°C and attempts were made to recharge the material at low temperatures (-20°C). The galvanostatic charge curves at 20°C for $\text{Cd}(\text{OH})_2$ showed little change after ageing apart from a less distinct demarcation between the end of charging and the onset of hydrogen evolution. At low temperatures (-20°C) pronounced Cd nucleation overpotentials were observed such that electrodes reached H_2 evolution at the start of charge. Potentiostatic

pulse experiments revealed no fundamental change in the mechanism of operation of the electrode.

Clearly, the growth of $\text{Cd}(\text{OH})_2$ leads to a marked reduction in its surface area which in turn leads to a lower rate of dissolution and difficulties in supplying soluble species required in the charge process. At low temperatures, where the solubility is drastically lowered, premature hydrogen evolution would be expected. The tendency of disordered $\text{Cd}(\text{OH})_2$ precipitates to undergo refinement of crystal quality with attendant loss in reactivity is a manifestation of the well-known Ostwald ripening process and reflects the inherent difficulty in maintaining thermodynamic free-energy gradients for long periods of time. It is perhaps fortunate that during the ageing process [73, 89] a large proportion of the active material within the sinter interior does not increase in size at the same rate as on the surface where there is a greater supply of free electrolyte. To date no satisfactory method has been found for entirely eliminating recrystallization of $\text{Cd}(\text{OH})_2$. Further work in this area is required to explore the possibility of metal hydroxide or organic compounds as a means of slowing down such processes.

In comparison nickel hydroxide electrodes, which operate entirely by a solid-state mechanism, showed little external morphological change after ageing [89] but exhibited even greater deterioration in electrochemical behaviour than the cadmium electrode. This is presumably due to the layer lattice of $\beta\text{-Ni}(\text{OH})_2$ undergoing increased ordering without the involvement of soluble intermediates.

Studies concerning the ageing of cadmium electrodes in silver–cadmium cells have been conducted by Papazova *et al.* [90]. According to these workers, after 12 months' storage at 20°C the metallic Cd particles had increased in size by at least an order of magnitude from 10^{-4} – 10^{-5} cm to 10^{-3} cm. It is claimed that the same relative increase in size could be induced after only six months' storage at 50°C . Similarly, after storage at 50°C an increase in $\text{Cd}(\text{OH})_2$ crystallite size was found from 10^{-4} cm after one month to 10^{-3} cm after 12 months.

Further studies [91] were conducted where anodes were stored at 20°C with a period at 40°C or 50°C . According to these workers whilst the Cd metal content could be observed to increase in size

after 2½ and 4 years, surprisingly no significant increase in size of Cd(OH)₂ crystallites was detected in the electrode interior.

Earlier studies by Yamashita and Yamamoto [92] have claimed that incorporation of antimony in the electrode structure can considerably retard the grain growth of metallic cadmium during long periods of storage. Cyclic voltammetric studies concerning the presence of antimony in the electrolyte were considered to show improvements in reversibility of the charge–discharge processes (cf. studies by Kadnikova *et al.* [38]).

5.2. Migration of Cd(OH)₂ and dendrite growth

An important cause of sealed cell failure or poor charge retention can arise from Cd metal growth through the separator. Such growth is usually considered to proceed via soluble cadmate present in the electrolyte. However, Mayer [93] has proposed that negatively charged Cd(OH)₂ particles can be transported electrophoretically through the separator. These results have been strongly criticized by several workers [94–96]. In a recent paper, Barnard *et al.* [96] have demonstrated that the increased solubility of cadmate at elevated temperatures can probably account for the presence of Cd(OH)₂ in the separator region.

The observation of Cd(OH)₂ crystallites in the separator region [89, 96, 97] has been advanced as evidence for short-circuit generation. However, it seems that the large well-formed hexagonal platlets are unlikely to recharge via a solid-state route and thus provide short circuits. Nevertheless their presence is undesirable because they provide a source of soluble cadmium species which may help the propagation of dendrites from certain points on the electrode surface.

Recently Sathyanarayana [98] has proposed the use of a nickel flash coating on the surface of the negative electrode to minimize Cd(OH)₂ and hence dendrite growth on the electrode surface. This nickel coating may also take part in the oxygen recombination reaction in the sealed cell and give further improvements in performance. Both ageing phenomena and the generation of Cd dendrites are a direct consequence of the operation of dissolution–precipitation reactions in the negative electrode, neither of which can be completely controlled.

5.3. Nickel–cadmium alloy formation

Levina and Rozentsveig [99] were the first to realize that nickel–cadmium alloy formation could take place between Ni(OH)₂ and Cd(OH)₂ during the charging process. It was demonstrated that the formation of γ -Ni₅Cd₂₁ was fairly rapid at high temperatures and at high electrolyte concentration. Alloy formation resulted in a step in the discharge curves at potentials about 150 mV more anodic than the normal Cd/Cd(OH)₂ discharge potential. Nickel hydroxide in varying amounts is usually present in sintered-plate electrodes because of corrosion of the nickel sinter during the impregnation process or as an additive to improve the cycle life of the plates [99, 100].

Pozin *et al.* [101] confirmed the earlier observations of Levina and Rozentsveig [99] and claimed that by application of a cathodic potential during the impregnation process the corrosion of nickel could be minimized and hence the level of nickel cadmium alloy. Pozin *et al.* [102, 103] have proposed the use of nickel–cadmium alloys prepared by heating the component metals at 300–400° C as an alternative to the conventional impregnated nickel sinter. It was found that γ -Ni₅Cd₂₁, γ_1 -Ni₂Cd₅ and β -NiCd could be produced. The first two materials are claimed to have the γ -brass structure whilst the third was considered to have the Ti₂Ni structure, but X-ray diffraction patterns were not presented. The cadmium-rich Ni₅Cd₂₁ tended to lose Cd at elevated temperature giving Ni₂Cd₅ and NiCd.

Pozin and Terentev [104, 105] have investigated the electrochemical behaviour of thermally produced nickel–cadmium alloys in 5.5 and 10 M KOH. According to these workers Ni₅Cd₂₁ and admixtures with Ni₂Cd₅ and NiCd have open-circuit potentials between –0.8 to –0.84 V compared with –0.86 to –0.9 V with respect to HgO/KOH for pure Cd. On discharge, all three alloys are claimed to discharge in the range –0.74 to –0.78 V; however, an additional low potential plateau is found at –0.2 to –0.4 V when Ni₂Cd₅ and Ni₅Cd₂₁ are also present. It is unlikely that the reversible potentials of the *pure* alloys are identical and the value obtained by the Soviet workers merely reflects a mixed potential in which the most active constituent, Ni₅Cd₂₁ dominates.

Similar behaviour occurs with Cd and $\text{Ni}_5\text{Cd}_{21}$ mixtures, the reversible potential being much closer to Cd even when fairly small levels of Cd are present. It would seem more likely that the additional low potential steps in the range -0.2 to -0.4 V are in fact due to discharge of the more noble phases rather than discharge of Ni to $\text{Ni}(\text{OH})_2$ as proposed by Pozin and Terentev [104, 105]. The latter process takes place near -0.8 V. Many of the interpretational difficulties in this paper appear to have arisen from the use of mixed phases.

Barnard *et al.* [34, 106] have similarly confirmed the earlier observations by Soviet workers regarding the formation of nickel-cadmium alloy in the negative plate during the charging process. Finely-divided Ni metal produced by reduction of up to 20% added $\text{Ni}(\text{OH})_2$ by Cd was found to form alloy more readily than the nickel sinter alone. The length of the secondary discharge plateau due to alloy discharge was dependent as expected on the $\text{Ni}(\text{OH})_2$ content, length of time in the charged state and also on temperature. For example, electrodes containing 20% $\text{Ni}(\text{OH})_2$ showed total conversion of active material to the alloy after charging for 1000 h at 75°C .

Samples of pure $\gamma\text{-Ni}_5\text{Cd}_{21}$ were obtained by electrochemical reduction of $\text{Ni}(\text{OH})_2/\text{Cd}(\text{OH})_2$ mixtures followed by a purification procedure. X-ray diffraction showed the alloy to have the cubic γ -brass structure [106] with a lattice parameter $a_0 = 8.574 \times 10^{-8}$ cm in good agreement with the crystal structure determined by Lihl and Buhl [107].

X-ray diffraction patterns for negative electrodes removed from sealed cells after trickle charging for 2 months at 75°C showed strong diffraction lines at $2\theta = 39.19^\circ$ (CuK_α radiation), highly characteristic of $\gamma\text{-Ni}_5\text{Cd}_{21}$ (cf. strong Cd line at $2\theta = 38.5^\circ$). Thus alloy formation was considered to be the cause of the stepped discharge curves also observed for sealed Ni-Cd cells under certain circumstances. Clearly such behaviour is undesirable because it leads to a loss in operating potential of more than 120 mV.

Attempts [106] to synthesize alloy phases other than $\text{Ni}_5\text{Cd}_{21}$ by electrochemical reduction of various $\text{Ni}(\text{OH})_2/\text{Cd}(\text{OH})_2$ mixtures were unsuccessful. When Cd was present in excess only $\text{Ni}_5\text{Cd}_{21}$ and Cd lines could be seen in the X-ray

patterns, conversely when Ni was in excess $\text{Ni}_5\text{Cd}_{21}$ and Ni lines were apparent. It was concluded at low temperatures ($25\text{--}75^\circ\text{C}$) that $\gamma\text{-Ni}_5\text{Cd}_{21}$ is the only phase present because all the diffraction lines could be attributed to this phase. Cyclic voltammetric studies [34, 106] showed that electrodes containing mixtures of Cd and $\text{Ni}_5\text{Cd}_{21}$ gave double anodic peaks related to the galvanostatic stepped discharge profile. On the other hand the pure alloy gave only a single peak displaced by about 120 mV from the normal Cd peak [106].

Equilibrium potential measurements showed that the cell $\gamma\text{-Ni}_5\text{Cd}_{21}/\text{Cd}(\text{OH})_2/30\% \text{KOH}/\text{HgO}/\text{Hg}$ had a value of -820 mV at 25°C in agreement with Pozin and Terentev [104, 105]. It is concluded that the lowering in potential during discharge arises from a corresponding lowering in free energy (~ 3.8 kcal/g atom) during alloy formation. Alternative causes for the stepped discharge profile such as discharge of absorbed hydrogen on the nickel sinter, surface blockage of $\text{Cd}(\text{OH})_2$ crystallites, or ohmic suppression due to a reaction distribution through the porous matrix could be entirely dismissed.

In a later paper Pozin *et al.* [108] investigated the electrochemical behaviour in 10 M KOH of mixtures of thermally produced Ni_2Cd_5 and $\text{Ni}_5\text{Cd}_{21}$ phases, and presented X-ray diffraction data for these phases. The pattern for $\text{Ni}_5\text{Cd}_{21}$ was in good agreement with that obtained by Barnard *et al.* [106] showing the characteristic line at $2\theta = 39.2^\circ$ (CuK_α radiation). The alloy phase Ni_2Cd_5 shows essentially only one strong line at $2\theta = 40^\circ$ the others being extremely weak. According to Pozin *et al.* [108] the mixed phase Ni_2Cd_5 and $\text{Ni}_5\text{Cd}_{21}$ has an open-circuit potential of -0.84 V with respect to $\text{HgO}/10$ M KOH. It is claimed that $\text{Ni}_5\text{Cd}_{21}$ is the most reactive phase and discharges at -0.75 V whilst the second step at -0.4 V corresponds only to Ni_2Cd_5 . There is some uncertainty as to whether the Ni_2Cd_5 component also discharges in the -0.75 V region. It is suggested that the discharge plateau at -0.4 V is abnormally low due to ohmic suppression and the true steady-state potential of Ni_2Cd_5 should be nearer -0.75 V. However, without measurements on pure Ni_2Cd_5 this assumption is difficult to verify as discussed previously. Certainly discharge of the more noble

alloy, Ni_2Cd_5 , would be expected at a lower potential than for $\text{Ni}_5\text{Cd}_{21}$.

In addition to the claim by Pozin *et al.* [102, 103] a German patent [109] also proposes the use of nickel–cadmium alloys, because of their fine state of subdivision, for use as the negative electrode in button cell systems. The alloy obtained by thermal decomposition of nickel and cadmium formates in a stream of hydrogen is claimed to be identifiable with the Hume–Rothery γ -phase $\text{Ni}_5\text{Cd}_{21}$. However, the X-ray evidence presented proposes a tetragonal crystal structure with lattice parameters $a_0 = 5.56 \times 10^{-8}$ cm and $b_0 = 6.08 \times 10^{-8}$ cm and is clearly incompatible with the well-established γ -brass structure [106–108]. The tetragonal lattice proposed (no diffraction data are presented) would require a diffraction line at $2\theta = 38.6^\circ$ (CuK_α radiation).

More recently Yasuda *et al.* [110] have investigated the formation of nickel–cadmium alloy in charged negative electrodes stored for periods of up to 2 years in sealed cells on open circuit. The sintered-plate negative electrodes contained $\sim 6\%$ $\text{Ni}(\text{OH})_2$ introduced by corrosion of the nickel sinter. Due to the extensive self-discharge of the plates in the sealed cell only small quantities of active material remained undischarged. This gave rise to poorly defined X-ray diffraction patterns for the alloy phase. After 2 years' storage a single discharge plateau at ~ -750 mV with respect to Hg/HgO was found together with a weak diffuse peak at $2\theta = 39.6^\circ$ (CuK_α) considered to be due to $\text{Ni}_5\text{Cd}_{21}$, but other peaks for this phase were not resolved. Upon re-charging the product after 2 years' storage both Cd metal and $\text{Ni}_5\text{Cd}_{21}$ peaks could be observed, the latter being slightly better resolved than immediately after storage and appearing at $2\theta = 39.2^\circ$. If the product after 2 years' storage was completely discharged before recharging then insufficient time was allowed for alloy reformation and the alloy peaks were absent as well as the low potential step. Barnard *et al.* [34] have similarly demonstrated that the secondary discharge step diminishes with rapid charge–discharge cycling.

At variance with the studies of other investigators [103, 104, 106, 108] the Japanese workers maintain that the alloy discharges in the range -890 to -880 mV as well as at -750 mV with respect to $\text{Hg}/\text{HgO}/\text{KOH}$. This confusing conclusion

is based on analytical measurements which claim to show release of $\text{Ni}(\text{OH})_2$ during discharge along the first plateau where only Cd metal discharge is thermodynamically possible. Furthermore, these workers consider that the Ni:Cd ratio found in the second plateau is 1:3 rather than 5:21. There appears to be considerable discrepancy between the delivered capacities and those calculated from the analytical values. These large differences cannot be accounted for in terms of absorbed hydrogen as suggested by Yasuda *et al.* [110].

The Japanese workers also propose that an alloy phase in addition to $\text{Ni}_5\text{Cd}_{21}$ may be present after 2 years' storage because of the single diffraction line at $2\theta = 39.6^\circ$ showing a superficial resemblance to that for Ni_2Cd_5 ($2\theta = 40^\circ$) presented by Pozin *et al.* [108]. However, even when the alloy diffraction line appears at $2\theta = 39.2^\circ$ the other lines characteristic of $\text{Ni}_5\text{Cd}_{21}$ are still absent. In view of the uncertainty in the analytical measurements by Yasuda *et al.* [110] it is likely that only a disordered $\text{Ni}_5\text{Cd}_{21}$ phase is present showing extinction of most diffraction lines. The Ni_2Cd_5 phase described by the Soviet workers [102, 103, 108] was obtained only at elevated temperatures and the possibility of its formation at room temperature seems unlikely.

5.4. Memory effect

'Memory effect' is a vague term used to describe a temporary loss in capacity or voltage when nickel–cadmium cells are subjected to precisely controlled charge–discharge cycles [111–114]. The effect manifests itself usually in the form of a voltage step of about 120 mV on discharge [113, 114] and is most noticeable after cells have been trickle charged at elevated temperatures. Because the memory effect can be temporarily erased by completely discharging followed by rapid recharging of the cell the effect is often not considered to be serious.

Nevertheless the memory effect was undesirable in the NASA space flight programme [111] and remains equally troublesome for standby applications such as emergency lighting. Until recently the most likely cause of the memory effect was uncertain, but in view of the known behaviour of nickel–cadmium alloys discussed in Section 5.3 the connection seems obvious.

Although a hysteresis effect is found for the positive electrode due to shifts in reversible potential the effect is not responsible for the stepped discharged curves [106]. The view previously held [113, 115] for the memory effect was that it was related to growth of Cd or Cd(OH)₂ causing ohmic suppression. Studies [34, 73] have shown that the discharge potential for electrodes exhibiting large Cd or Cd(OH)₂ crystallites is normal in the absence of Ni₅Cd₂₁. Furthermore the stepped discharge profile can be present when large Cd(OH)₂ crystallites are entirely absent and very little Cd/Ni₅Cd₂₁ growth has taken place [74].

Yasuda *et al.* [110] have similarly concluded in agreement with Barnard *et al.* [34, 106] that carbonate contamination of the electrolyte or Cd(OH)₂ crystal growth cannot be the prime cause of the low potential discharge plateau.

6. Theoretical studies concerning porous Cd electrodes

Relatively advanced theoretical models to describe the operation of porous cadmium electrodes have been proposed. However, these still do not account fully for the known experimental characteristics of the system. Complications arise because of non-uniform distribution of concentration, current and active material within the electrode which change throughout charge–discharge cycling.

Models to account for the shape of the potential–time curves and their dependence on current density have invariably involved pore blocking and restricted diffusion of soluble species. Casey and Vergette [116] consider that Cd utilization on discharge involves cadmium in three distinct regions: surface, larger pore lining and micropore. The latter material is claimed to be available only at extremely low rates of discharge. A ‘choking index’ was defined, being small when the free pore volume was large and *vice versa*. Will [117] has considered the development of pH gradients within the porous electrode during charge and discharge. The local concentration cells formed between regions of different pH allow current to flow along the pores and this in turn is responsible for the non-uniform current distribution within the sinter. Such an effect could also contribute to the progressive redistribution of active material during cycling.

Bro and Kang [118] have examined the reaction profiles in compressed Cd powder electrodes at various current densities and have proposed an empirical equation to describe the polarization behaviour. The overpotential was found to be very strongly dependent on current density. Przybla *et al.* [119] have similarly developed empirical equations relating discharge efficiency of the cadmium electrode at various temperatures to the current density, electrode thickness and anode porosity.

In a more recent series of papers Dunning *et al.* [120–123] have developed a detailed model for the operation of electrodes involving sparingly soluble reaction products such as Cd/Cd(OH)₂. Both solid-state (continuous-film) and dissolution–precipitation modes of electrode failure are considered. The dissolution–precipitation model takes into account the mass transfer limitations of soluble species and the changes in volume between the Cd and Cd(OH)₂. The solubility of active material is shown to impose a practical limit on the mass transfer parameters. A mass transfer coefficient is defined which depends on diffusion rates and rates of crystallization or nucleation of active material as well as the fraction of free Cd surface. These workers also attempted the difficult task of taking into account the redistribution of active material within the pores during charge–discharge cycling, a feature neglected in previous treatments.

The model proposing electrode failure via a continuous film showed the potential changing gradually (almost linearly) with time and did not predict a rapid cut-off of potential as found experimentally. On the other hand the model involving partial blockage of the surface by precipitated anodic products showed the potential to increase rapidly after a certain time. Dunning *et al.* [120–123] conceded that neither model separately could describe accurately the behaviour of the cadmium electrode on discharge and a combination of processes was likely to be involved.

Selanger [124] has developed a model to describe the behaviour of porous electrodes at very high current densities. A one-dimensional pore model as used by previous workers was used to predict the shape of the overpotential–time transients at various current densities and the influence of electrode thickness and porosity. Electrode failure at low current densities was considered to be

caused entirely by blockage of pores whilst at high rates mass transfer limitation was considered to predominate. The possibility of passivation via a solid-state mechanism was neglected. Transition from a pore blockage to a mass transfer limitation was considered to occur at $100\text{--}200\text{ mA cm}^{-2}$ at a porosity of $\sim 60\%$.

Equations [125] were also proposed to predict the shape of potential–time curves during pulse discharge at high rates where mass transfer was considered to be the only limiting feature. Accordingly the Nernst equation was used to predict the changes in potential arising from changes in the activity of the electrolyte.

From a consideration of the molar volumes of the active material Selanger [126] considers that the $\text{Fe}/\text{Fe}(\text{OH})_2$ system is most sensitive to changes in electrode porosity whilst $\text{Cd}(\text{OH})_2$ is least sensitive. In a further paper [127] the interrelation between electrode thickness and porosity on the efficiency of utilization of active material was discussed. At high rates the highest efficiency is given by plates having a high porosity but only an intermediate thickness (i.e. not the thinnest plates).

Recently Micka *et al.* [128] derived equations to describe the potential–time behaviour of porous cadmium electrodes during galvanostatic discharge. These equations take detailed account of the mass transfer of ionic electrolyte species within the plates and the change of porosity during discharge. However, the model assumes complete reversibility of the electrode process and the equation describing the variation of the potential of the Cd electrode on discharge incorporates a term only for the activity changes of water in the pores. This treatment neglects the influence of supersaturation of soluble cadmium species and rates of nucleation and crystallization of $\text{Cd}(\text{OH})_2$. At short times and high current densities these effects may be important and would cause the e.m.f. to fall more rapidly than proposed by the model. It is significant that Micka *et al.* [128] find lower discharge times at higher current densities than predicted by the model. However, this departure is considered to be due to a critical current density being reached such that the potential changes to -0.88 V with respect to $\text{Hg}/\text{HgO}/\text{KOH}$ to allow a solid-state reaction to proceed (cf. Armstrong *et al.* [68]). The critical point occurs at a shorter time with thin electrodes.

Thus the efficiency of utilization is found to increase with electrode thickness at the expense of increased concentration overpotential. Consequently, as discussed also by Selanger [127], a compromise must be sought regarding electrode thickness and concentration polarization.

Current distribution diagrams for the porous Cd electrode were obtained by Micka *et al.* [128] which were similar to those obtained by Bro and Kang [118]. It may be recalled that both groups of workers use essentially a pressed Cd powder electrode fabrication. According to Micka *et al.* [128] even at the low current densities used by Bro and Kang [118] electrode passivation would be predicted. Micka *et al.* demonstrate however, at very low current densities, that the Cd electrode approaches 100% efficiency and the electrode is not passivated. Pore blockage is similarly unimportant. The abrupt increase in polarization at moderate rates is attributed to both passivation and to a decrease in electronic conductivity of the active material.

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